

# Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope geothermometer

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## Abstract

Although commonly utilized in continental geothermal work, the water–hydrogen and methane–hydrogen isotope geothermometers have been neglected in hydrothermal studies. Here we report  $\delta\text{D-CH}_4$  and  $\delta\text{D-H}_2$  values from high-temperature, black smoker-type hydrothermal vents and low-temperature carbonate-hosted samples from the recently discovered Lost City Hydrothermal Field. Methane deuterium content is uniform across the dataset at  $-120 \pm 12\text{‰}$ . Hydrogen  $\delta\text{D}$  values vary from  $-420\text{‰}$  to  $-330\text{‰}$  at high-temperature vents to  $-700\text{‰}$  to  $-600\text{‰}$  at Lost City. The application of several geothermometer equations to a suite of hydrothermal vent volatile samples reveals that predicted temperatures are similar to measured vent temperatures at high-temperature vents, and 20–60 °C higher than those measured at the Lost City vents. We conclude that the overestimation of temperature at Lost City reflects 1) that methane and hydrogen are produced by serpentinization at  $>110$  °C, and 2) that isotopic equilibrium at temperatures  $<70$  °C is mediated by microbial sulfate reduction. The successful application of hydrogen isotope geothermometers to low-temperature Lost City hydrothermal samples encourages its employment with low-temperature diffuse hydrothermal fluids.

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*Keywords:* Lost City; Hydrogen isotope geothermometer; Sulfate reduction; Hydrothermal vents

## 1. Introduction

The fortuitous discovery of the Lost City Hydrothermal Field (LCHF) in 2000 (Kelley et al., 2001) may represent the most significant paradigm shift in hydrothermal studies since the initial sighting of black smokers in 1979 (Spiess et al., 1980). Located 15 km west of the Mid-Atlantic Ridge axis, Lost City's towering carbonate chimneys are interpreted to be the seafloor expression of an active, non-magmatic, low-

temperature hydrothermal system (Kelley et al., 2001). Unlike a prototypical mid-ocean ridge hydrothermal system where circulation is driven by an underlying magmatic heat source, Lost City is propelled by exergonic reactions between seawater and ultramafic rocks (Früh-Green et al., 2003; Kelley et al., 2005). In addition to supplying heat beneath Lost City, these serpentinization reactions are the main determinant of the fluid chemistry and volatile content.

Here we utilize the temperature dependent fractionation of hydrogen isotopes between water–hydrogen and methane–hydrogen to determine isotopic equilibrium temperatures. We present data from a variety of hydrothermal vent sites from around the ocean basins, including samples from slow-, intermediate-, and fast-

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spreading ridges, as well as sedimented and unsedimented ridges. Special attention is paid to the Lost City Hydrothermal Field due to its unique geologic context, low-temperature venting of high pH, metal-poor fluids, and extremely depleted hydrogen isotopic signature.

The geothermometers implemented in this study are based on theoretical calculations by Bottinga (1969) and Richet et al. (1977), and experimental work by Suess (1949) and Horibe and Craig (1995). While the utility of  $\text{H}_2\text{O}-\text{H}_2$  and  $\text{CH}_4-\text{H}_2$  isotope geothermometers has been demonstrated in continental geothermal work (Abrajano et al., 1988; Arnason, 1977; Coveney et al., 1987; Fritz et al., 1992; Lyon and Hulston, 1984; Neal and Stanger, 1983; Sherwood Lollar et al., 1993), these geothermometers have not been rigorously applied to submarine hydrothermal vent environments. Except for several measurements from the  $21^\circ\text{N}$  vent site on the East Pacific Rise (EPR) (Horibe and Craig, 1995; Welhan and Craig, 1983),  $\delta\text{D}$  analyses of hydrothermal  $\text{CH}_4$  and  $\text{H}_2$  are rarely reported in the literature. The limited application of hydrogen isotope geothermometers to submarine hydrothermal studies may be due to the apparent lack of information contained in the data from  $21^\circ\text{N}$ . In this initial study the geothermometer-predicted temperatures matched the measured vent fluid temperatures ( $\sim 350^\circ\text{C}$ ) (Horibe and Craig, 1995; Welhan and Craig, 1983). The measurements and calculations presented herein from high-temperature hydrothermal

vents support the original conclusion that isotopic equilibrium is established during fluid ascent. However, the low-temperature fluids venting at Lost City require a different explanation, as the hydrogen isotope geothermometers calculate temperatures  $20\text{--}60^\circ\text{C}$  higher than those measured at the vent orifice. The application of  $\text{H}_2\text{O}-\text{H}_2$  and  $\text{CH}_4-\text{H}_2$  isotope geothermometers to Lost City samples reveals valuable information about the reaction conditions and formation temperatures of the volatiles at this unique vent site.

## 2. Geologic setting

Samples used in this study include deep-sea hydrothermal sites from around the globe: Endeavour, Middle Valley, Guaymas, EPR at  $9^\circ\text{N}$ , Central Indian Ridge, Broken Spur, Logatchev, and Lost City (Fig. 1). The Endeavour site is composed of five vigorously venting black smoker fields located on the Juan de Fuca Ridge, classified as an intermediate-spreading center, in the Northeast Pacific. While Endeavour is observed to be unsedimented, it has many chemical signatures of a sedimented hydrothermal system (Delaney et al., 1992; Lilley et al., 1993; Proskurowski et al., 2004; You et al., 1994). Middle Valley, located 40 km north and east of Endeavour, is covered by thick (300–1500 m) terrigenous sediment, and is the site of several Ocean Drilling Project drill holes (Butterfield et al., 1994; Goodfellow et al., 1987; Whittaker et al., 1994). Guaymas, located

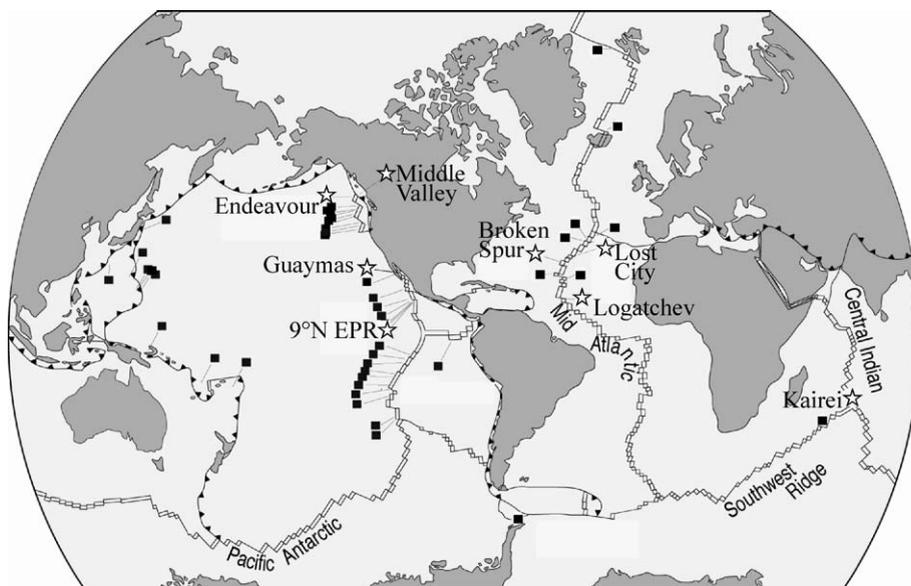


Fig. 1. Sample locations. Hydrothermal volatile samples (open stars) selected from vent sites along ultra-slow-, slow-, intermediate-, and fast-spreading ridges; sediment- and bare-rock-hosted environments; and Lost City, an off-axis site of hydrothermal circulation driven largely by serpentinization. Solid squares represent sites of known hydrothermal venting. Unmodified figure provided by Timothy Shank (WHOI).

along the segment of the EPR that extends into the Gulf of California, is a high-temperature hydrothermal site rooted in, and heavily influenced by, pelagic sediments (Von Damm et al., 1985; Welhan and Lupton, 1987). The vents located at 9°N along the EPR are commonly regarded as the prototypical, fast-spreading basalt-hosted hydrothermal system (Fornari and Embley, 1995; Fornari et al., 1998; Von Damm et al., 1995). The Kairei vent field on the Central Indian Ridge is an intermediate spreading center that lies on the eastern rift-valley wall, directly north of the Rodriguez Triple Junction (Van Dover et al., 2001). Both Broken Spur and Logatchev are vent sites located on the slow-spreading Mid-Atlantic Ridge (MAR), however, Broken Spur is a basalt-hosted system while a mixture of basalt, gabbro, and ultramafic rocks is exposed at the surface at Logatchev (Charlou et al., 2002; Douville et al., 2002; James et al., 1995). Lost City, located ~15 km west of the MAR on 1.5 my old crust, is an ultramafic-hosted low-temperature hydrothermal system. Circulation at this site is driven by heat derived from exothermic serpentinization reactions and cooling of the lithosphere, rather than by purely magmatic processes (Kelley et al., 2001;

Kelley et al., 2005). Vents at this site are characterized by unusually tall (up to 60 m) carbonate structures, venting relatively cool (20–91 °C), basic (pH 9–11) metal-poor fluids. The field contains ~15 known large towers and covers an area 100×200 m (Fig. 2) (Früh-Green et al., 2003; Kelley et al., 2001; Kelley et al., 2005).

### 3. Methods

All high-temperature fluid samples were obtained between 1991 and 2000 using gas-tight titanium samplers (Edmond et al., 1992) with the submersible *Alvin* or robotic vehicle *Jason*. Lost City was revisited in April 2003 for a comprehensive study consisting of 19 *Alvin* dives and a nightly Autonomous Benthic Explorer (ABE) program (Kelley et al., 2005). During this expedition ~60 gas-tight samples of fluids from eight different active vents were recovered. The samplers are specifically designed to prevent the loss of volatiles if degassing occurs as a result of cooling during ascent from the seafloor (Edmond et al., 1992). Upon shipboard arrival the sample is transferred from the gas-tight sampler into an evacuated gas-manifold

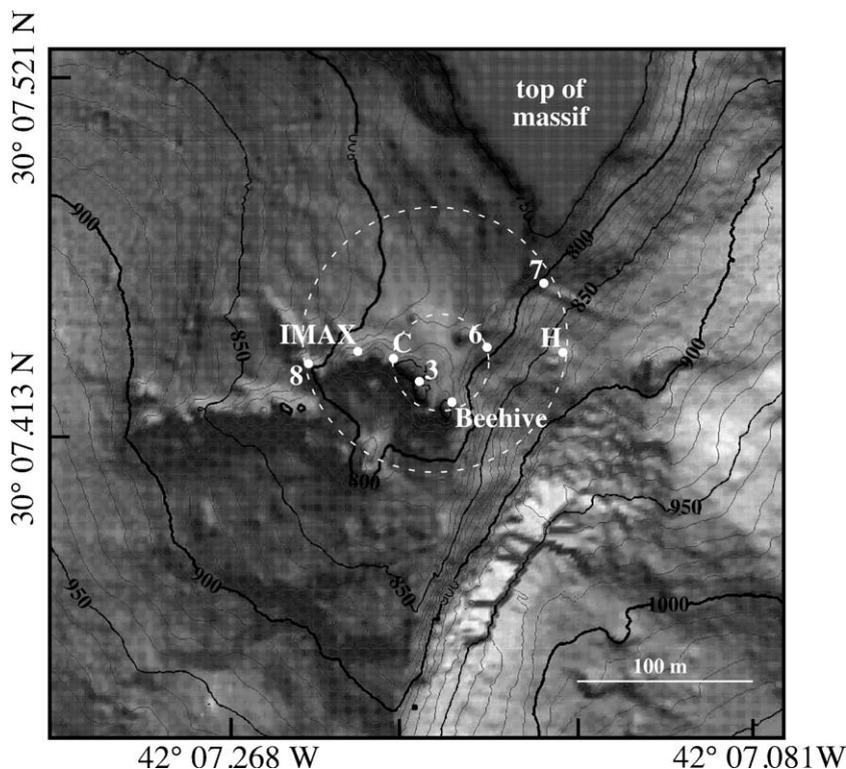


Fig. 2. Lost City Hydrothermal Field. Bathymetric map of the Lost City Hydrothermal Field showing vent locations. The small dotted circle highlights vents 3, 6, C and Beehive (BH), located near the center of the field. These sites have higher hydrogen concentrations and temperatures than vents 7, 8, IMAX (IF) and H, situated further afield and outlined by the large dotted circle. A model invoking chemical, geological and microbiological processes is presented herein to explain the geographical distribution of chemically distinct vent fluids.

vacuum line. The gas is stripped from the fluid through the addition of acid and ultrasonic agitation, dried using a  $-60\text{ }^{\circ}\text{C}$  water trap, and total gas is measured manometrically. Multiple aliquots are flamed off into breakseal ampoules, which are archived and stored for on-shore analysis. The fluid fraction of the sample is preserved for later analysis of major anions and cations.

The concentrations of archived gas samples were determined using gas chromatography techniques. All concentrations reported here represent endmember values and are corrected for small amounts of seawater inevitably entrained during sampling. Magnesium is the standard seawater indicator in hydrothermal studies, and measured values are extrapolated to a 0 mmol/kg Mg, “pure vent fluid”, value. Samples were prepared for gas chromatography-isotope ratio mass spectrometric (GC-IRMS) analysis of  $\delta\text{D-H}_2$  and  $\delta\text{D-CH}_4$  by first expanding whole gas fractions into a small ( $\mu\text{l}$ – $100\text{ }\mu\text{l}$ ) valved volume. The apparatus containing the sample was then mounted on a custom-built inlet system in-line with the GC-IRMS, the dead volumes were purged with He carrier gas, and the sample was swept into the carrier stream. Before introduction to the GC, the sample was cryofocused under liquid nitrogen temperatures for 3 min at the head of a 15 m, 0.53 mm MXT-PLOT mol sieve column to insure quantitative sample capture. A slight temperature ramp was applied to the column, and after separation the peaks were pyrolyzed in-line at  $1440\text{ }^{\circ}\text{C}$ . Water was removed via an in-line Nafion membrane, and the peaks, as pulses of pure hydrogen gas, were inlet to a continuous flow Thermo-Finnigan MAT 253 mass spectrometer. All hydrogen isotope values are reported in the conventional per mil (‰) notation with reference to Vienna Standard Mean Ocean Water (VSMOW). Standard mixtures of  $\text{CH}_4$  and  $\text{H}_2$  with independently determined isotopic values were subjected to the same treatment as samples in order to calibrate the results with respect to VSMOW. Samples were measured in triplicate and values represent the mean value of multiple analysis. Analytical error, as determined by repetitive analysis of multiple standards, varied between 2–6‰ for  $\delta\text{D-H}_2$  and 5–10‰  $\delta\text{D-CH}_4$ .

The measured hydrogen isotope values for  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  were evaluated to find the equilibrium fractionation factor. Here, we explicitly define the equilibrium fractionation factor,  $\Delta$ , using the standard convention:

$$\Delta_{\text{A-B}} = 1000\ln\alpha_{\text{A-B}} \quad (1)$$

where  $\alpha_{\text{A-B}} = \frac{R_{\text{A}}}{R_{\text{B}}}$  for any isotope ratio  $R$  ( $^{13}\text{C}/^{12}\text{C}$ , D/H, etc.).

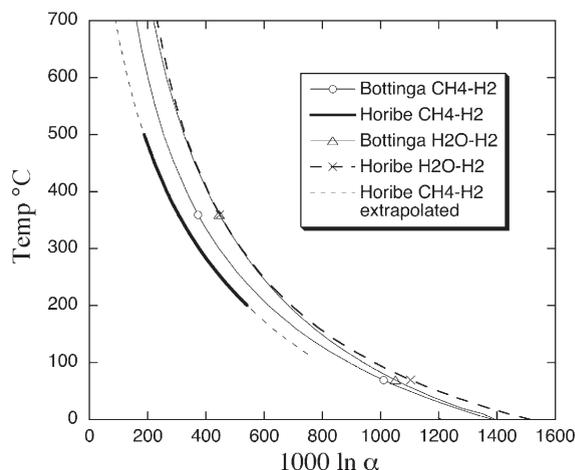


Fig. 3. Comparison of hydrogen isotope geothermometers. The geothermometers employed herein predict temperature based on theoretically (Bottinga, 1969) and experimentally determined (Horibe and Craig, 1995) equilibrium isotopic fractionations between  $\text{CH}_4$  and  $\text{H}_2$ , and  $\text{H}_2\text{O}$  and  $\text{H}_2$ . The  $\text{H}_2\text{O-H}_2$  geothermometers are in good agreement between 100 and  $500\text{ }^{\circ}\text{C}$ . Temperatures predicted by the Horibe and Craig,  $\text{CH}_4\text{-H}_2$  geothermometers are lower than those predicted by the Bottinga geothermometer. The Horibe and Craig  $\text{H}_2\text{O-H}_2$  geothermometer should be considered the most robust, as it is experimentally determined, and the kinetics of  $\text{H}_2\text{O-H}_2$  equilibration is favorable when compared to  $\text{CH}_4\text{-H}_2$ . The extrapolation of the Horibe and Craig  $\text{CH}_4\text{-H}_2$  geothermometer is based on a similar treatment in Friedman and O’Neil (1977).

It should be noted that defined this way, a positive  $\Delta_{\text{A-B}}$  value indicates species B is isotopically depleted with respect to species A. We calculate temperature from the fractionation factor using the data and equations in Bottinga (1969) and Horibe and Craig (1995) (Fig. 3).

## 4. Results and discussion

### 4.1. General trends of D/H data

The hydrogen isotope compositions of methane and hydrogen were measured for approximately 30 samples, and are presented in Table 1. Hydrothermal  $\text{CH}_4$   $\delta\text{D}$  values range between  $-140\text{‰}$  and  $-95\text{‰}$ . There is no discernable trend between  $\delta\text{D-CH}_4$  and methane concentration, but there is a weak relationship between  $\delta\text{D-CH}_4$  and measured vent temperature; the majority of Lost City samples fall between  $-140\text{‰}$  to  $-120\text{‰}$  and the majority of high-temperature vent samples range from  $-120\text{‰}$  to  $-95\text{‰}$  (Fig. 4). The  $\sim 45\text{‰}$  variation in  $\delta\text{D-CH}_4$  is small compared to that for  $\delta\text{D-H}_2$ , which ranges from  $-700\text{‰}$  to  $-330\text{‰}$ . The hydrogen isotope concentration of measured hydrothermal  $\text{H}_2$  samples is linearly related to measured vent fluid temperatures

Table 1  
Hydrogen isotope geothermometer data

Location	Measured vent $T$ (°C)	E.M. $H_2$ (mmol/kg)	E.M. $CH_4$ (mmol/kg)	$\delta D-H_2$ (‰)	$\delta D-CH_4$ (‰)	$^aH_2O-H_2$ 1000ln $\alpha$	$H_2O-H_2^b$ Bottinga $T$ (°C)	$H_2O-H_2^c$ Horibe $T$ (°C)	$CH_4-H_2$ 1000ln $\alpha$	$CH_4-H_2^b$ Bottinga $T$ (°C)	$CH_4-H_2^c$ Horibe $T$ (°C)
LC-BH	90	8.97	1.03	-609.2	-126.6	944	102	115	804	131	98
LC-BH	90	9.22	1.07	-609.2	-125.8	943	102	115	805	130	97
LC-IF	55	3.69	1.21	-648.8	-128.6	1050	70	87	909	101	68
LC-IF	55	3.35	1.14	-645.5	-138.5	1041	73	90	888	107	73
LC-IF	55	3.77	1.28	-648.4	-135.7	1049	70	88	899	104	70
LC-6	67	14.14	1.61	-604.8	-107.7	932	106	118	814	128	95
LC-6	62	14.19	1.55	-615.9	-128.8	961	97	110	819	126	93
LC-7	28	5.54	1.29	-662.8	-129.3	1091	58	77	949	90	57
LC-7	28	5.43	1.31	-666.0	-124.5	1101	56	74	964	86	53
LC-8	43	4.20	1.84	-657.5	-141.4	1075	63	81	919	98	65
LC-8	43	4.10	1.79	-650.5	-136.0	1055	69	86	905	102	69
LC-C	62	7.90	1.07	-620.0	-126.1	971	93	108	833	122	89
LC-C	70	14.38	1.98	-613.9	-130.1	956	98	112	812	128	95
LC-H	60	2.21	1.44	-656.8	-99.1	1073	63	81	965	85	53
LC-H	60	0.90	1.34	-689.4	-103.6	1173	37	56	1060	60	31
LC-3	61	11.58	1.26	-610.4	-111.6	947	101	114	824	125	92
LC-3	71	13.26	1.55	-604.8	-103.1	932	106	118	819	126	93
LC-3	73	11.94	1.30	-608.6	-125.0	942	103	115	804	131	98
Broken Spur	353	1.59	0.11	-392.6	n.m.	499	313	315	n.d.	n.d.	n.d.
Logatchev	350	19.03	3.99	-372.4	-109.3	466	341	344	350	385	321
9N	380	12.98	0.09	-328.2	n.m.	398	412	417	n.d.	n.d.	n.d.
SWIR	350	8.17	0.19	-400.0	n.m.	511	303	304	n.d.	n.d.	n.d.
Middle Valley	274	6.20	8.00	-415.9	-110.2	538	283	284	421	316	269
Middle Valley	285	5.44	5.26	-423.7	-106.6	551	273	274	438	301	258
Guaymas	317	3.16	52.01	-379.3	-95.9	477	331	334	376	358	301
Endeavour	375	0.48	2.58	-345.0	-125.1	423	384	388	289	460	376
Endeavour	375	1.38	2.02	-331.9	-107.1	403	405	411	290	460	375
Endeavour	341	0.14	1.25	-386.7	n.m.	489	321	323	n.d.	n.d.	n.d.
Endeavour	340	0.12	1.17	-356.6	n.m.	441	365	369	n.d.	n.d.	n.d.
Endeavour	338	0.24	2.08	-379.5	n.m.	477	331	333	n.d.	n.d.	n.d.
21N EPR <sup>d</sup>	350	0.95	0.02	-388.0	-114.0	491	319	321	370	364	306
Oman <sup>d</sup>	35	n.m.	n.m.	-715.0	-240.0	1255	18	37	981	81	49
Zambales <sup>d</sup>	n.m.	n.m.	n.m.	-585.0	-128.0	n.d.	n.d.	n.d.	743	150	118

E.M. = endmember. n.m. = not measured. n.d. = not determined.

<sup>a</sup>  $\delta D-H_2O$  values for Lost City measured at 2–7‰, assumed to be 0‰ for high-temperature sites.

<sup>b</sup> (Bottinga, 1969).

<sup>c</sup> (Horibe and Craig, 1995).

<sup>d</sup> 21°N (Welhan and Craig, 1983), Oman (Fritz et al., 1992), Zambales (Abrajano et al., 1988).

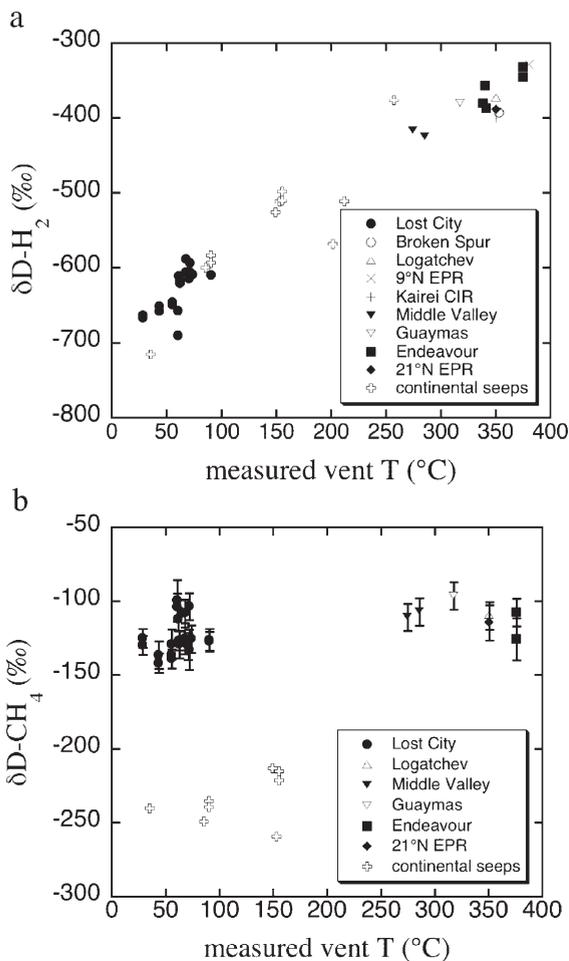


Fig. 4.  $\delta\text{D-H}_2$  and  $\delta\text{D-CH}_4$  vs. measured vent temperature. Stable hydrogen isotopic composition of (a) hydrogen and (b) methane plotted vs. measured vent temperature from selected vent sites. Original data except from 21°N EPR (Welhan and Craig, 1983) and continental seeps (Oman (Fritz et al., 1992), New Zealand (Lyon and Hulston, 1984), Zambales (Abrajano et al., 1988), Cerro Prieto (Welhan, 1981), Iceland ( $\text{H}_2$  only, Arnason, 1977) and Yellowstone (Welhan, 1981)). The  $\sim 400\%$  range in  $\delta\text{D-H}_2$  is strongly related to measured vent temperature. As the  $\delta\text{D-H}_2\text{O}$  and  $\delta\text{D-CH}_4$  values for submarine hydrothermal fluids are relatively constant ( $\sim 0\%$  and  $-150$  to  $-100\%$ ), the geothermometer-predicted temperature of hydrothermal fluids is largely a function of  $\delta\text{D-H}_2$ . The  $\pm 4\%$  error associated with original  $\delta\text{D-H}_2$  measurements is less than the width of the plotting symbol.

(Fig. 4). This is evident where high-temperature fluids with  $\delta\text{D-H}_2$  ranging from  $-420\%$  to  $-330\%$  are enriched relative to low-temperature Lost City fluids that range from  $-700\%$  to  $-600\%$ . While there is no apparent correlation between  $\text{H}_2$  concentration and  $\delta\text{D-H}_2$  at high-temperature vents (Fig. 5), at Lost City increased  $\text{H}_2$  concentrations are consistent with enriched  $\delta\text{D-H}_2$  values. The relationship between  $\text{H}_2$ , temperature and  $\delta\text{D-H}_2$  will be developed later, but illustrates the important result that

temperature is a key determinant in hydrogen production at Lost City.

The  $\delta\text{D}$  values of  $\text{CH}_4$  are similar to those from hydrothermal vents at 21°N along the EPR ( $-126\%$  to  $-102\%$ ) (Welhan and Craig, 1983) and gas seeps at the Zambales Ophiolite ( $-136\%$ ) (Abrajano et al., 1988). They are enriched relative to geothermal gases from New Zealand ( $-197\%$  to  $-142\%$ ) (Lyon and Hulston, 1984), the Canadian Shield ( $-372$  to  $-133$ ) (Sherwood Lollar et al., 1993), and methane from seeps in the Oman ophiolite ( $-251\%$  to  $-210\%$ ) (Fritz et al., 1992).

The wide range of  $\delta\text{D-H}_2$  values presented here encompasses most reported values from previous hydrothermal and geothermal studies. Hydrogen from 350 °C fluid at 21°N is reported to have  $\delta\text{D-H}_2$  values of  $-410\%$  to  $-388\%$  (Horibe and Craig, 1995; Welhan and Craig, 1983), which is in the center of the range that we report for high-temperature fluids. The depleted Lost City  $\delta\text{D-H}_2$  values are similar to low-temperature seep sites in exposed sections of ancient oceanic crust such as the ophiolites in Zambales ( $-590\%$ ) and Oman ( $-699\%$ ) (Abrajano et al., 1988; Abrajano et al., 1990; Fritz et al., 1992). The deuterium content of  $\text{H}_2$  from continental geothermal sites of intermediate or variable temperatures falls within the range measured in this study e.g.  $-630\%$  to  $-360\%$  at 174–266 °C Icelandic thermal areas (Arnason, 1977),  $-450\%$  to  $-130\%$  in Canadian Shield boreholes (Sherwood et al., 1988), and  $-600\%$  to  $-310\%$  from 160–240 °C geothermal fluids in New Zealand (Lyon and Hulston, 1984).

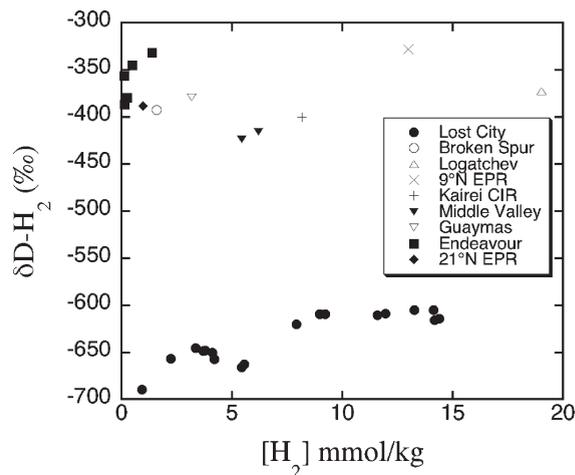


Fig. 5.  $\delta\text{D-H}_2$  vs. endmember  $\text{H}_2$  concentration. The range in hydrogen concentration at Lost City is nearly as large as that observed from a wide selection of hydrothermal sites. Lost City fluids are  $\sim 300\%$  depleted in  $\delta\text{D-H}_2$  relative to high-temperature black-smoker sites.

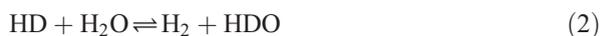
#### 4.2. Utility of D/H geothermometer

Both Lyon and Hulston (1984) and Arnason (1977) applied hydrogen isotope geothermometers to their data with successful results: isotopically predicted temperatures were similar, or slightly elevated, when compared to temperature estimations from dissolved silica. The ~310 °C predicted temperatures for 21°N fluids by Horibe and Craig (1995) are in decent agreement with the predicted regional base temperature of 350 °C. These studies employed isotope geothermometers based on the equations of Bottinga (1969) and Richet et al. (1977), which are assumed to be robust between 0 and 700 °C. Horibe and Craig (1995) slightly modified the equations by incorporating experimental data between 200 and 500 °C. We extrapolate the experimentally derived geothermometer equations to accommodate the low-temperature Lost City samples, a treatment similar to the one published in Friedman and O'Neil (1977). Fig. 3 illustrates the differences and similarities between the geothermometers used in this study. A brief examination of the geothermometers explains the large spread in  $\delta\text{D-H}_2$  values and relatively constant  $\delta\text{D-CH}_4$  values. The  $\text{H}_2\text{O-CH}_4$  geothermometer (Bottinga, 1969) depends very little on temperature (~60‰ fractionation over 400 °C) whereas the  $\text{H}_2\text{O-H}_2$  and  $\text{CH}_4\text{-H}_2$  geothermometers are strongly temperature dependent (~1000‰ fractionation over 400 °C).

Several caveats should be noted regarding the use of  $\text{H}_2\text{O-H}_2$  and  $\text{CH}_4\text{-H}_2$  isotope geothermometers in this study. First, the error associated with isotopic measurements propagates into the geothermometer calculations. Thus, temperature predictions have an error of  $\pm 5\text{--}10$  °C for  $\text{H}_2\text{O-H}_2$  calculations and  $\pm 10\text{--}15$  °C for  $\text{CH}_4\text{-H}_2$  calculations; lower errors are associated with the larger isotope fractionations of low-temperature samples. Second, the  $\delta\text{D}$  of  $\text{H}_2\text{O}$  was not explicitly measured for all high-temperature samples presented here, however we assume it to be  $0\pm 3\text{‰}$  based on previously reported values (Shanks et al., 1995). Lost City waters have  $\delta\text{D}$  values of  $+2\text{‰}$  to  $7\text{‰}$  (Früh-Green, personal communication), and are slightly more enriched in deuterium than waters in black smoker hydrothermal systems (Shanks et al., 1995). Third, the isotope geothermometer calculations are based on theoretically or experimentally determined equilibrium isotope fractionations, and therefore only apply under equilibrium conditions. At lower temperatures, there exists the possibility that the  $\text{H}_2\text{O-CH}_4\text{-H}_2$  system is no longer in isotopic equilibrium. If this is true, the calculated temperatures reflect the temperature at which the fluid was last in isotopic equilibrium. Lastly,

the viability of the isotope geothermometers at low temperatures is still under evaluation. While this study demonstrates the utility of hydrogen isotope fractionation to predict temperature in a variety of hydrothermal environments, potentially sluggish kinetics at low temperatures could complicate the results. Experimental studies at low temperature examining the rates and magnitude of isotopic exchange would be valuable in determining the robustness and suitability of the geothermometers used here.

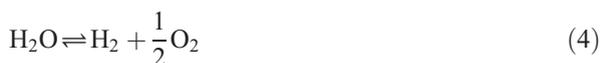
Isotopic equilibrium for the  $\text{H}_2\text{O-H}_2$  geothermometer is established via the overall reaction:



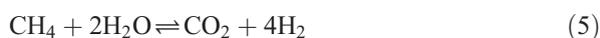
and isotopic equilibrium in the  $\text{CH}_4\text{-H}_2$  system can be expressed by:



Isotopic equilibrium implies that chemical equilibrium for these reactions has been reached. However, the chemical pathways for reaching the equilibrium indicated in reactions (2) and (3) are likely more complex. It is possible that chemical, and possibly isotopic equilibrium, may be achieved via reactions such as:



and



Chemical equilibrium between hydrogen and water is likely established via the general reaction (4), as has been concluded in experimental and theoretical hydrothermal modeling studies (Seyfried and Ding, 1995). Previous stable carbon isotope investigations of site-specific hydrothermal methane and carbon dioxide conclude that these species are not in isotopic equilibrium at temperatures of ~400 °C (Kelley and Früh-Green, 2001; Shock, 1990; Welhan and Craig, 1983). While methane and carbon dioxide may not be in equilibrium isotopically, the extent of chemical equilibrium is currently not known. A systematic review of all known vent fluids may reveal that equilibrium has been established chemically under hydrothermal conditions.

Presently, the kinetics of hydrogen isotope exchange reactions are poorly constrained. The rates for uncatalyzed  $\text{H}_2\text{O-H}_2$  and  $\text{CH}_4\text{-H}_2$  isotopic exchange reactions are sluggish at temperatures less than 200 °C. One of the primary reasons that Horibe and Craig (1995) do not present  $\text{CH}_4\text{-H}_2$  isotope exchange data for temperatures less than 200 °C is that the sluggish kinetics of

the reaction at low temperature does not allow for exchange during a reasonable study period, even under catalyzed conditions. At 200 °C metal catalyzed  $\text{CH}_4\text{-H}_2$  isotopic exchange occurred after experimental periods of 1–50 hours (Horibe and Craig, 1995). Incubation times of 1–2 hours are sufficient for Pt-catalyzed  $\text{H}_2\text{O-H}_2$  exchange reactions to occur at room temperature (Horita, 1988). Equilibration times of tens to hundreds of hours is much longer than the time scale expected for upwelling fluid moving through a conduit (vent flow rates estimated at 1 m/s (Schultz and Elderfield, 1999)), but may be similar to the residence times of fluids in the hot root zone (Kadko and Butterfield, 1998). In the absence of appropriate mineral or metal catalysts and temperatures below 300 K isotopic equilibrium occurs extremely slowly, with  $\text{H}_2\text{O-H}_2$  exchange occurring slightly more rapidly than  $\text{CH}_4\text{-H}_2$  exchange (Lecluse and Robert, 1994). Whether isotope exchange is facilitated by mineral and metal catalyst, or simply the combination of high temperatures and long periods of time, it is clear that  $\text{H}_2\text{O-H}_2\text{-CH}_4$  isotopic equilibrium is established in hydrothermal and geothermal systems of temperatures greater than  $\sim 200$  °C (Arnason, 1977; Horibe and Craig, 1995; Lyon and Hulston, 1984; Welhan and Craig, 1983), and perhaps as low as 50 °C (Neal and Stanger, 1983).

#### 4.3. D/H geothermometer applied to high-temperature hydrothermal systems

The results of four hydrogen isotope geothermometer calculations are shown against the measured vent temperatures in Fig. 6. The  $\text{CH}_4\text{-H}_2$  geothermometers bracket the range of calculated temperatures, with the Bottinga (1969) equations predicting temperatures 30–60 °C higher than the Horibe and Craig (1995) geothermometer. The two  $\text{H}_2\text{O-H}_2$  calculations yield similar results, with the predicted temperatures commonly bisecting the range defined by the  $\text{CH}_4\text{-H}_2$  computation. When applied to hydrothermal systems, the Horibe and Craig  $\text{H}_2\text{O-H}_2$  geothermometer should be considered the most robust geothermometer of the four geothermometers discussed here. The Horibe and Craig  $\text{H}_2\text{O-H}_2$  geothermometer describes isotope fractionations between liquid water and hydrogen (as opposed to Bottinga's water vapor–hydrogen calculations) and combines experimental (Cerrai et al., 1954; Suess, 1949) and theoretical (Bardo and Wolfsberg, 1976) fractionation determinations over a temperature range appropriate to hydrothermal systems. Black-smoker-type high-temperature vents exhibit a 60 °C difference between the two  $\text{CH}_4\text{-H}_2$  geothermometer calculations. However, the mean of the  $\text{CH}_4\text{-H}_2$  calculated temperatures, as well as the predicted

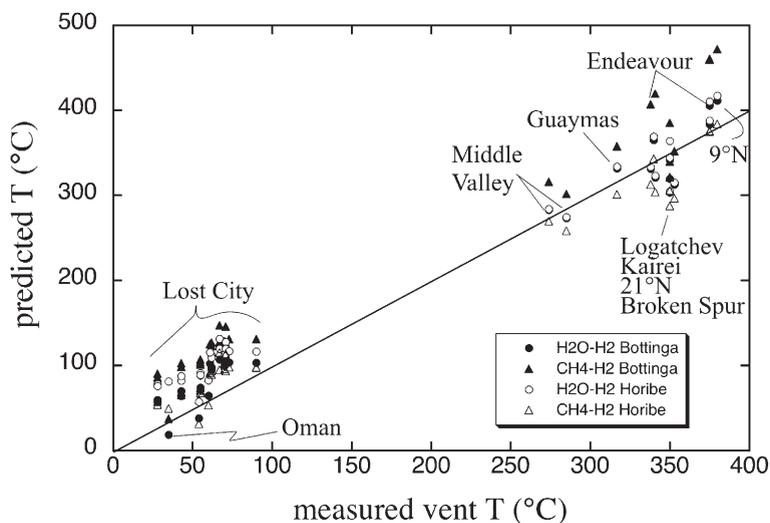


Fig. 6. Geothermometer results vs. measured vent temperature. Predicted temperatures from four hydrogen isotope geothermometers plotted against measured vent temperature. As mentioned in the text, the  $\text{H}_2\text{O-H}_2$  Horibe and Craig geothermometer (open circles) should be considered the most robust of the four presented here. Notice that, for every sample, the Horibe and Craig  $\text{H}_2\text{O-H}_2$  geothermometer-predicted temperature is within 5 °C of the median predicted temperature when considering all four geothermometers. The line (slope=1) represents a predicted temperature that exactly matches the measured temperature. At temperatures  $>250$  °C the  $\text{H}_2\text{O-H}_2$  geothermometer-predicted temperature approximates the measured temperature. At Lost City, measured vent temperatures are less than what would be expected from the hydrogen isotopes. Geothermometer results indicate serpentinization reaction temperatures of at least 110 °C.

H<sub>2</sub>O–H<sub>2</sub> temperatures, consistently approximates the measured vent fluid temperature. This result, that the isotope geothermometer calculated temperature reflects the measured temperature for high-temperature samples, is similar to the conclusions from studies in Iceland and 21°N (Arnason, 1977; Horibe and Craig, 1995). It appears that at high-temperature vents the volatile species dissolved in the fluid are in isotopic equilibrium, essentially to the sampling point, and thus the measured isotopic fractions reflect the venting temperature. While it is reassuring that the geothermometer predictions agree with the measured temperature, new information is not stored in the hydrogen isotopes of high-temperature samples.

#### 4.4. D/H geothermometer applied to the Lost City Hydrothermal Field

In contrast to the high-temperature systems, geothermometry within low-temperature environments does not accurately predict effluent temperatures at the vent sites. However, geothermometry does provide information about processes in the upflow zone. Hydrogen isotope data from the low-temperature Lost City vents indicate that the fluids have cooled during ascent to the seafloor, as geothermometer-predicted temperatures are consistently 20–60 °C greater than measured venting temperatures. The geothermometer temperature reflects the temperature at which the H<sub>2</sub>-bearing species would have been last in isotopic equilibrium. As shown in Fig. 8, the Lost City data fall into two groups: a moderate-

temperature (average of 70 °C) and high hydrogen concentration group (10.5 mmol/kg), and a low-temperature (average of 45 °C) and low hydrogen concentration group (3.7 mmol/kg). The higher-temperature vents have an average isotope-predicted temperature of 110 °C, and the low-temperature vents are calculated to be 73 °C.

The significant H<sub>2</sub> concentrations at Lost City are produced by serpentinization, a process that hydrolyzes mafic or ultramafic rock to create serpentinite, heat, and hydrogen. A theoretical model of the Lost City system predicts that serpentinization occurs at 200±50 °C (Allen and Seyfried, 2004), overlapping with ~185 °C temperatures predicted by δ<sup>18</sup>O–CaCO<sub>3</sub> measurements on carbonate veins in basement peridotites. However, the absence of anhydrite precipitation at Lost City, as well as δ<sup>18</sup>O–CaCO<sub>3</sub> evidence from active and extinct chimneys, suggests that temperatures of fluids exiting at the seafloor are at no point greater than 150 °C (Kelley et al., 2005). Serpentinization reactions can progress at temperatures as low as 100 °C, but reaction rates are much faster at higher temperatures, especially between 200 and 300 °C (Martin and Fyfe, 1970). The data presented here corroborate the conclusions drawn from fluid chemistry that serpentinization occurs at Lost City under low-temperature (<150 °C) conditions (Kelley et al., 2005).

At Lost City, the geothermometers record a temperature of 110 °C for samples venting at 70 °C, even though several samples are consistent with isotopic equilibrium at temperatures less than 70 °C (Fig. 7).

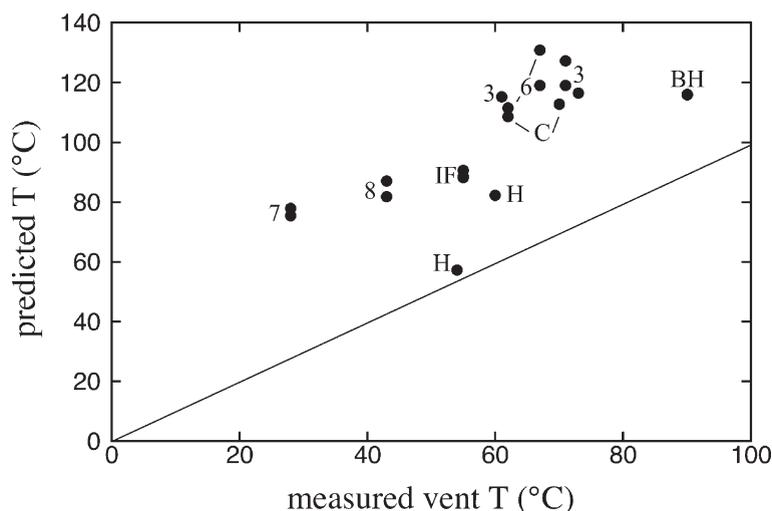


Fig. 7. Horibe and Craig H<sub>2</sub>O–H<sub>2</sub> geothermometer results at Lost City. The Horibe and Craig H<sub>2</sub>O–H<sub>2</sub> geothermometer-predicted temperature at Lost City plotted against measured vent temperature. The line depicts a 1:1 ratio between predicted and measured temperature. The data fall into two groups: 3, 6, C, and BH have predicted temperatures 100–130 °C, and 7, 8, IF, and H have predicted temperatures 45–85 °C.

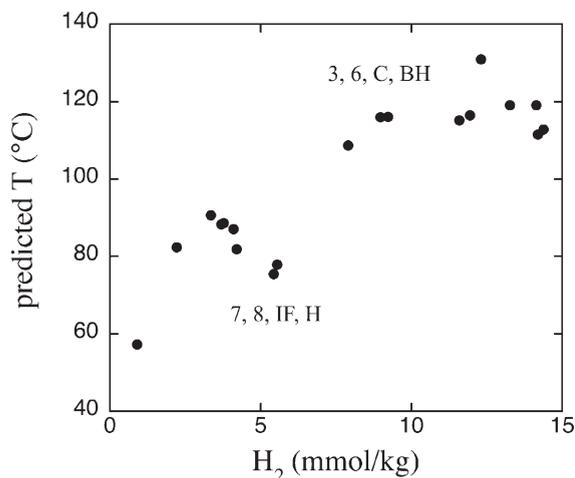


Fig. 8. Horibe and Craig  $\text{H}_2\text{O}-\text{H}_2$  predicted temperature vs. endmember hydrogen concentration. The Horibe and Craig  $\text{H}_2\text{O}-\text{H}_2$  geothermometer-predicted temperature plotted against endmember hydrogen concentration at Lost City reveals an unambiguous grouping of high-hydrogen/moderate-temperature and low-hydrogen/low-temperature fluids. Referring back to Fig. 2, high-hydrogen/moderate-temperature sites are located towards the center of the LCHF while the low-hydrogen/low-temperature vents are more distally situated. Conductive cooling, seawater mixing, and microbial sulfate reduction in fractures that move fluid away from a central conduit feeding vents 3, 6, C, and BH may explain the low hydrogen concentrations and low predicted temperatures of 7, 8, IF and H vents.

These results indicate that cooling of the fluids occurs more rapidly than the rate of equilibrium isotopic exchange. We envision a model where hydrogen is produced during serpentinization reactions in the basement under temperatures of 110–150 °C. At depth, the fluids are then slowly cooled to 70–110 °C while maintaining isotopic equilibrium, and then rapidly conductively cooled during ascent to the seafloor. It should be noted that cooling does not occur by the mixing of hydrothermal fluid and cold seawater because the endmember compositions of venting fluids do not show the chemical tracers of seawater (e.g. bicarbonate or magnesium) (Kelley et al., 2005). Subsurface cooling by seawater mixing, with subsequent precipitation of carbonate minerals (thus removing magnesium and bicarbonate) is unlikely as very small amounts of magnesium are present in the chimneys and underlying veins at Lost City (either in the mineral matrix of carbonate or as brucite) (Kelley et al., 2005).

The spatial distribution of the vent sites at Lost City suggests a relationship between the moderate-temperature/high-hydrogen and the low-temperature/low-hydrogen samples. The high-temperature sites (Marker 3, Marker C, Beehive, and Marker 6) lie in a narrow (75 m)

zone centered on the primary feature at Lost City, Poseidon. This tower is an actively venting 60 m tall carbonate structure. The low-temperature sites (Marker H, Imax Flange, Marker 8, and Marker 7) are located 80–100 m from the central spire, lying towards the outer edges of the field (Fig. 2). We imagine that a cylindrical zone of serpentinization extending deep beneath Poseidon could serve to insulate fluid near the center of the conduit and allow for cooler temperatures towards the margins. However, the establishment of a stable reaction zone is unlikely because the volume expansion associated with serpentinization destroys the local porosity, and the alteration of fresh ultramafic rock requires vast quantities of unaltered rock, especially considering the >30,000 year lifetime of the Lost City field (Früh-Green et al., 2003; Kelley et al., 2001). Furthermore, five-fold changes in hydrogen production due to slight changes in serpentinization temperature have not been experimentally observed. The shortcomings of a purely geological explanation for the dichotomous Lost City hydrogen and temperature values beg for additional justification. A likely control on the hydrogen concentrations observed at Lost City is microbiological sulfate reduction using  $\text{H}_2$  as an electron donor.

Endmember sulfate concentrations at Lost City range from 1 to 4 mmol/kg, and are positively correlated with hydrogen concentration and inversely correlated with total sulfide concentration (Kelley et al., 2005). Systematic variations in hydrogen, sulfate and sulfide abundances are consistent with thermophilic microbial sulfate-reducing metabolisms that anaerobically consume sulfate and hydrogen to produce sulfide (Butterfield et al., 2004; Jannasch, 1995; Jorgensen et al., 1992; Jorgensen et al., 1990). Active microbial sulfate reduction at Lost City is evidenced by the presence of bacterial sequences associated with Firmicutes, a sulfate-reducing phylotype, as well as traces of lipid biomarkers specific to sulfate reducers (glycerol mono- and diethers with saturated and unsaturated  $\text{C}_{15}-\text{C}_{20}$  *n*-alkyl chains) (Kelley et al., 2005).

Sulfate- and iron-reducing bacterial metabolisms have been observed to facilitate isotopic equilibrium between water and  $\text{H}_2$  at low temperatures (Romanek et al., 2003). Analysis of the hydrogen headspace above active cultures of the thermophilic sulfate-reducing bacteria *D. luciae* yielded extremely depleted  $\delta\text{D}-\text{H}_2$  values corresponding to  $\text{H}_2\text{O}-\text{H}_2$  fractionation at the growth temperature (Romanek et al., 2003). Romanek et al. (2003) hypothesize that activity of the enzyme hydrogenase in effect catalyzes hydrogen isotope exchange, to temperatures as low as 30 °C. Thus, while Lost City vent fluids with high hydrogen

concentrations are kinetically inhibited from reaching isotopic equilibrium at temperatures less than  $\sim 100$  °C, isotopic exchange at low-hydrogen/low-sulfate vents may be catalyzed by bacterial sulfate reduction. In this case the isotopes record temperatures as low as 56 °C.

Based on these results, we hypothesize a model that incorporates 1) coupled serpentinization processes and fracture-determined flow channels to constrain temperature and 2) microbiologically mediated sulfate reduction that results in variable hydrogen concentrations, and H<sub>2</sub>O–H<sub>2</sub> isotopic exchange at temperature less than 100 °C. Beneath the Lost City field, serpentinization reactions in the basement rocks occur at temperatures of 110–150 °C within an anastomosing network of small cracks. These reactions produce a fluid of fairly uniform chemical composition that is rich in hydrogen and methane. Concomitant with mineral–fluid reactions, the fluids are progressively heated through exothermic processes and from lithospheric cooling. The now buoyant fluids rise and coalesce along progressively larger cracks and are channeled towards the surface. Intersection of upwelling fluids with large, through-going faults directs the flow to the center of the Lost City Hydrothermal Field, resulting in the hottest vents with the highest volatile content. Secondary channels disperse a portion of the fluid away from the largest central conduits. During this process the fluids are conductively cooled. It is in these cooler fluids that sulfate-reducing bacteria actively consume hydrogen and facilitate isotopic equilibrium. The result is that vents located away from Poseidon are low in hydrogen concentration and have isotopic temperatures lower than measured temperatures at high-hydrogen vents proximal to Poseidon.

## 5. Conclusions

Gas-tight fluid samples from a variety of hydrothermal vent sites worldwide were analyzed for the deuterium composition of hydrogen and methane. Isotopic equilibrium temperatures were calculated using H<sub>2</sub>O–H<sub>2</sub> and CH<sub>4</sub>–H<sub>2</sub> geothermometer equations as determined by Bottinga (1969) and Horibe and Craig (1995). The isotope-predicted temperatures of high-temperature fluids ( $>275$  °C) were, across the board, similar to the measured venting temperature, despite the environmental diversity of the sample locations. The results from high-temperature fluid samples presented here indicate that the kinetics of isotope exchange are rapid enough at black-smoker hydrothermal conditions that isotopic equilibrium is established essentially to the sampling point at the seafloor. This result confirms the

conclusions of the initial study of hydrothermal hydrogen isotope geothermometry (Horibe and Craig, 1995). While these results do not provide any new insight into the temperature structure of high-temperature hydrothermal systems, they affirm the utility of the geothermometers employed.

Measurements from low-temperature fluids at the Lost City Hydrothermal Field yield geothermometer-predicted temperatures 20–60 °C higher than measured temperatures. Although rates of isotopic exchange are believed to be slow at Lost City vent temperatures, we believe that active microbial sulfate reduction results in isotopic equilibrium in several of the  $\sim 70$  °C venting fluids. We interpret the  $\sim 110$  °C temperatures calculated from isotopic analyses of samples taken from the most vigorously venting sites to be the minimum temperature of serpentinization. Serpentinization under low-temperature conditions and volatile production at Lost City does not require heat extraction from a magmatic source, demonstrating that proximity to a ridge axis is not necessary to establish hydrothermal circulation. While Lost City is the only off-axis serpentinite-hosted vent field yet discovered, seafloor exposures of serpentinized peridotite are a common feature along fracture zones associated with slower spreading mid-ocean ridges (Dick et al., 2003; Früh-Green et al., 2004). Lost City-type hydrothermal systems have the potential to be as widespread in seafloor serpentinite exposures as black smokers are along mid-ocean ridges. The intriguing information resulting from the application of isotope geothermometers to the low-temperature Lost City data encourages the measurement of hydrogen isotopes in other low-temperature environments such as areas of diffuse flow that support biological communities, and argues for the experimental examination of isotope exchange at low temperature.

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